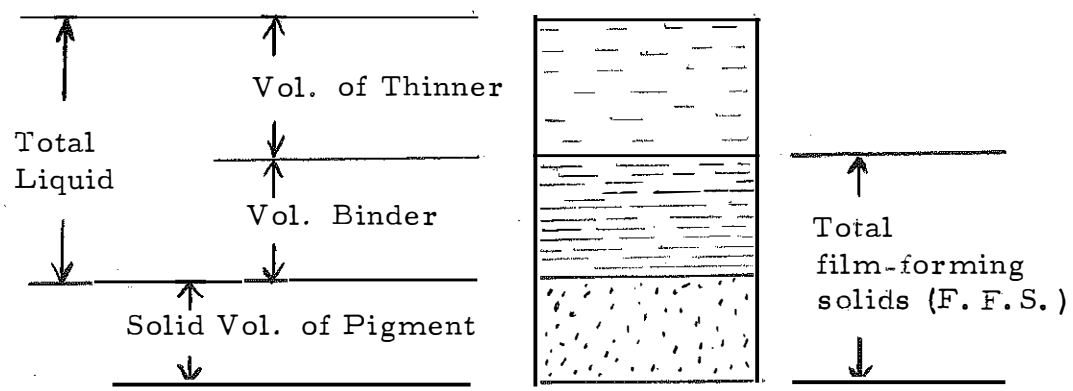
FUNDAMENTAL PRINCIPLES IN PAINT TECHNOLOGY

(Jas. H. Havens)

There are certain fundamental volumetric relationships which should be observed in designing and formulating paints for various uses. A gallon of paint, for instance, equals 231 cu. in.: Assume then that a particular paint contained 25% volatile solvent or thinner by volume, 213 x 25% = 58 cu. in.; 231 - 58 = 173 cu. in., which is the volume of film-forming solids (F. F. S.). If this paint is applied to a non-absorptive, smooth surface and it covers 500 sq. ft., then the wet film thickness would be: 231 cu. in. / (500 x 144) = .0032 inches (3.2 mils), and the film thickness after drying would be: 231 - 58 / (500 x 144) = .0024 in. (or 2.4 mils). Thus the amount of volatile solvent and spreading rate of the paint govern the thickness of the dry paint film.

Volume-wise, a gallon of paint may be visualized according to the following diagram:



Note: $\frac{\text{P. V.}}{\text{F. F. S.}}$ = P. V. C. (Pigment Vol. Concentration)

Solvent or thinners are necessary to obtain the desired consistency and workability, but the combined volume of pigment and binder represents the volume of film-forming solids (F.F.S.) available from each gallon of paint. There are, in addition to this, important relationships between the volume of pigment and volume of the binder which should be observed in designing paints. Gloss, for instance, is achieved by the complete submergence of all pigment in the binder when the paint has been applied and dried. Thus the volume of binder should be greater than the bulk volume of pigment. In flat or non-glossy paints, the pigment particles should protrude through the binder; and, therefore the volume of binder should be slightly lower than the bulk volume of pigment. This relationship is conveniently and customarily expressed as pigment volume concentration (P.V.C.). It is simply the volume of pigment per volume of film-forming solids:

$$\text{P.V.C. (\%)} = \frac{\text{Solid Volume of Pigment}}{\text{Volume of F.F.S.}} \times 100$$

Note: $\text{Solid Vol. (gal.)} = \frac{\text{Wt. in Lbs.}}{\text{Sp. G} \times 8.33}$

P. V. C. for flat paints usually ranges between 55% and 67%, semi-glosses - 39% to 58%, glosses - 28% to 47%, and enamels - 17% to 35%. In a two-coat system, P.V.C. for the undercoat should range between 37% and 32% and between 35% and 40% for the finished coat. A one-coat hiding, refinish paint (defined later) should range between 35% and 40% P.V.C. These design values may represent general averages, whereas the actual

performance of such paints as well as the textures achieved will vary somewhat with the condition of the surfaces to which they are applied, absorption of vehicle, and pigment packing factors.

Since the design value of P.V.C. more-or-less establishes the volume of total pigment, this means that all of the hiding power of the paint must be contained within a limited range of pigment volume. This may be easier to understand after first considering the pertinent factors involved in the design and evaluation of hiding power. The Hallet System provides a convenient method of designating and assessing the hiding qualities of mixed paints. Hiding power, then, is based on the ratio of the hiding power of 1 lb. a pigment to that of 1 lb. of basic carbonate white lead (1 H. U. per lb.). Thus, if 26 hiding units per gallon of paint is considered the very minimum that would provide complete one-coat hiding of 450 to 500 sq. ft. of area, such a paint would have to contain 26 lbs. of basic carbonate white lead per gallon. This pigment has a specific gravity of 6.70, and 26 lbs. of it would have a solid volume of .062 cu. ft., 107 cu. in., or .464 gal. If the remaining volume were made up entirely of binder, the P.V.C. would be 46.4%. However, if it were found that 20% volatile thinner by volume was required to produce a brushing consistency, this would displace .20 gal. of binder from each gallon of paint (preserving 26 hiding units) and would reduce the actual volume of film-forming solids to 1 gal. - .2 gal. solvent = .8 gal., of which .464 gal. would be made up of pigment. In this case, then, P.V.C. = .464/.8 x 100 = 58% which is still within the range accepted for flat, non-glossy paints; but such a

paint would be extremely heavy and rather expensive. If the lead carbonate cost 17-1/2 cents/lb., 26 lbs., at 17-1/2 cents = $4.55.

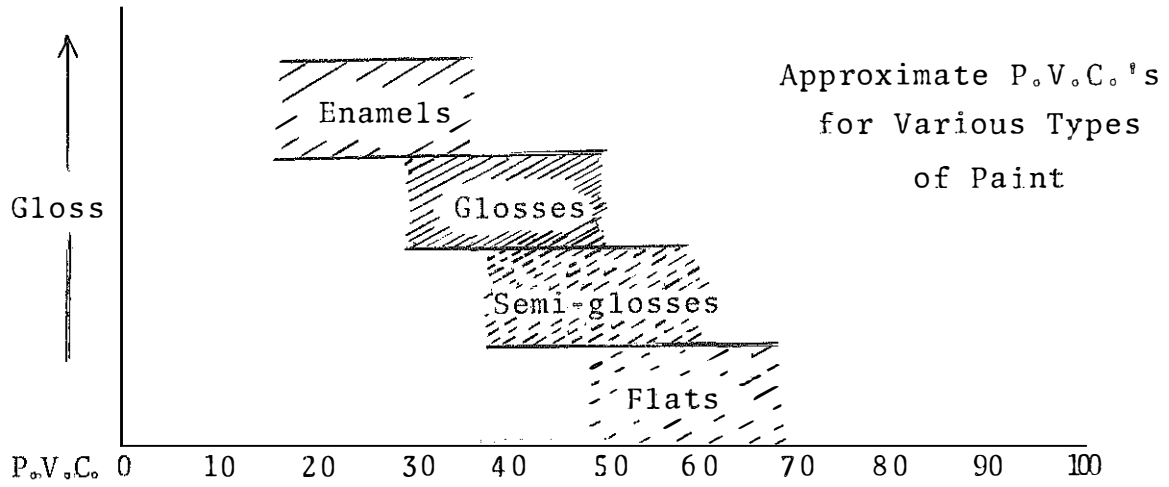
In contrast, if the pigmentation were made up entirely of Titanium Rutile which has 8.16 times more hiding power than the white lead, 26 hiding units could be provided by 3.2 lbs. of total pigment. If this pigment cost 27-1/2 cents/lbs.; 3.2 x 27-1/2 cents = $ .87. The Rutile has a specific gravity of 4.2, and 3.2 lbs. would provide only 21.1 cu. in. or .092 gal. of solid volume.

$$P.V.C. = \frac{.092}{.8} \times 100 = 11.4\%$$

This value does not agree with the P.V.C. criteria for any of the types of paint mentioned earlier, and it can now be seen that blending of prime pigments with extenders is usually necessary in order to achieve a balanced design which will take into account both hiding power and P.V.C. Pigment extenders, which are credited with no hiding power, may, of course, be used advantageously in conjunction with high hiding-strength pigments to provide the necessary bulk (solid volume), or hiding-strength pigments blended with low or medium strength pigments with or without extenders may be used to achieve the desired balance. ((Note: Tables showing pounds per gallon and gallons per pound (bulking values) for various paint ingredients are appended at the end of this section.))

In house paints, 2 to 4 mils dry thickness are considered necessary for adequate protection against the ingress moisture. However, house paints should be designed to be self-cleaning and therefore must

undergo slow but controlled chalking (erosion). This means that a properly designed paint system should provide the necessary moisture barrier plus a reserve thickness to take into account a number of years of normal erosion. Suppose a house is given two coats of paint totaling 4.8 mils dry thickness and the normal erosion rate is 0.4 mil per year, in two or three years the paint may become vulnerable to moisture and thereafter may become susceptible to rapid deterioration. Had 6 mils been applied, the paint would have had about 5 years of expected life, after which it could be entirely revitalized by the applicztion of a single finish coat with a minimum of spot priming. Programmed re-painting is therfore an essential part of long-range maintenance. If re-paint work is done too frequently or without due allowance of time for normal erosion, the accumulation of paint becomes too thick, too brittle, and may crack, wrinkle, and peel. This could eventually necessitate removal of all the existing paint and unnecessarily require a complete re-paint job.



Drying Oils and Oil-Resin Vehicles

Selectivity in type of vehicle is governed largely by the use and purpose for which the paint is intended. Drying-oil vehicles are more suited to exterior work since they require air and sunlight for proper drying. Soluble resin vehicles are particularly well suited for interior applications since they harden by evaporation of the solvent. Oil-modifications of resin vehicles for exterior or interior paints provide some control of over excessive penetration of the vehicle into the surface, brittleness, toughness, impermeability, shrinkage, and even brushing characteristics. Compatibility between undercoats and finish coats depends largely upon the type of vehicles used and P.V.C. A straight alkyd-type finish coat over a drying-oil under-coat may result in "aligatoring" or wrinkling of the finish coat due to unequal drying and shrinkage.

For many years, white lead and raw linseed oil (usually 100 lbs. white lead, 2 gals. linseed oil, 2 gals. turpentine, and 1 pt. drier) was used in three or more coats for house painting. White lead has rather low hiding power but favors the formation of a soft film and promotes good adhesion. Attempts to replace the white lead with white zinc oxide resulted in rather extreme harding, embrittlement, and even complete loss of film adhesion. Now it is known that the lead pigments reacted with organic acids introduced with the raw linseed oil, or generated by weathering, to form water-insoluble lead soaps which gave the film plasticity and strong adhesion. Zinc pigments, on the other hand, strengthened and hardened the film but also reacted to form water-soluble soaps which

account for the tendency to loose adhesion. Thus, in modern house paint formulas, the larger quantities of leaded pigment (35 to 45%) are relegated to under-coats and the zinc pigment (25 to 30% ZnO or leaded zinc) to outer finish coats. Additional hiding is usually obtained from other pigments such as those of the titanium type. Extender pigments may be used advantageously to provide bulk and toughness.

Raw linseed oil contains impurities in the form of water and non-drying fatty acids and glycerides which interfere with its film-forming properties (i.e. water resistance, toughness, etc.). Boiled linseed oil may be simply raw oil from which water and other equally volatile impurities have been eveporated away (heated to 150° F and air blown), or the term may refer to "bodied" linseed oil which has been thickened (polymerized) by prolonged cooking and air-blowing at temperatures in excess of 500°F. This cooking and "bodying" process is essentially the same process that takes place in the normal drying of the raw oil in a paint film. If the cooking is continued, the oil is eventually converted to a semi-solid resin or else is decomposed. For many purposes raw linseed oil is purified by treatments designed to remove a large portion of the non-drying oils and other impurities (about 10%) prior to "bodying". In this form it is usually termed "pure" or "refined" linseed oil, and it is superior in many respects to the raw oil. The "bodied" oil is better known as varnish oil which is cooked with resin and thinned to form varnishes and enamel vehicles. In the better drying-oil-type paints, however, the bodied pure oil comprises the major portion of the vehicle and is non-penetrating. Controlled penetration and leveling

characteristics are achieved by adding an appropraite amount of pure but "unbodied" oil. Therefore, a distinction in quality would be made between paints containing identical pigmentations but different types of vehicles.

Some General Features of Paints, Varnishes and Enamels

The simplest paint would be a mixture of drying oil, such as linseed oil, pigment, thinner such as turpentine, and possibly some drier. It has been stated previously that the primordial formula for house paint consisted of 100 lbs. of white lead (1.8 gal.) 2 gal. linseed oil, 2 gal. turpentine, and 1 pint. (0.125 gal.) drier.

Percent Volatiles, by Vol. ------ 33.7

Percent F.F.S., by Vol. ------- 66.3

Percent P.V.C. ---------- 47.5

Hiding Units, Per Gal., Hallet --- 17

Spreading at the rate of 1 gal. per 500 sq. ft. would give a wet film thickness of 3.2 mils and a dry thickness of 2.1 mils. Since at least 26 hiding units per 500 sq. ft. are required for complete hiding, at least two coats would be required; and there would not be much reserve hiding to allow for normal chalking. Two coats would, therefore, provide slightly more than the minimum foundation (26 hiding units and 4 mils dry thickness).

At present, there is a diverse multitude of paint-making materials: prime pigments, extenders, drying oils, resins, driers and thinners.

With due recognition and control given to P.V.C., hiding, and F.F.S., the matter of formulating paints is largely a problem of selecting ingredients to achieve a balance between performance and economy. There are, of course, certain guiding experience factors to be observed. There are choices as to prime and extender pigments and with respect to resins, blends of resins, bodied and unbodied oils, and thinners.

Varnish-like materials were known in ancient times. Spirit varnish, in its simplest sense, is an unpigmented solution of clear, polymerized, hard resin. The solvent or thinner is used to dissolve and liquify the resin for application. After application, the solvent evaporates, leaving the surface coated with a continuous film of resin; afterwards, they cannot be re-dissolved in the same type of solvents. Natural resins are obtained by drying the sap of some trees. Rosin, though not suitable as a varnish resin in its natural form, is the resin obtained from pine trees. Others are Manila, Zanzibar, Damar, Kauri, etc. named primarily by the port of origin but varying in character according to the species of the trees. Amber and some others are fossil resins of ancient species of trees.

The varnish trade does not regard rosin and shellac as natural resins and frequently refers to those natural resins as "gums". In strict terminology, however, the gums are related to sugars and carbohydrates. They are soluble in water, forming viscous solutions and are insoluble in drying oils and organic solvents. On heating they decompose without melting. For contrast, natural resins are insoluble in water, melt on heating and are generally soluble when cooked in vegetable oils and organic

solvents. They are chemically related to the terpenes.

Natural resins, in the pure or raw form are unduly brittle. Early varnishes of the 18th century were made by cooking natural resins in linseed oil, until thickened, and then diluting the mixture with a solvent such as turpentine. This was generally the composition of the early spar varnishes (long-oil, 25 to 30 or possibly as much as 50 gal. per 100 lb. of resin). Furniture varnishes were short-oil types (6 to 15 gal. per 100 lbs. of resin).

Raw, unrefined linseed oil is usually contaminated with water and glycerides of oleic and stearic acids which are like lard (10 to 15%), which do not dry themselves, and which interfere with the film-making characteristics of drying oils (glyceride of linoleic acid). Alkali refined, pure oils have had these contaminates removed. The refined, unbodied oil then has good wetting characteristics. With continued hearing at temperatures in excess of 500^{o}F, the oil thickens and becomes bodied. In this form it is usually known as varnish oil which, though used in paint vehicles too, is cooked with natural or synthetic resins and other drying oils to make varnishes and enamel vehicles.

Synthetic resins such as; phenol formaldehyde, alkyds, urea formaldehyde ester gums, melamines, epoxys, vinyls, and silicones are now much in demand for varnish making.. Chinawood oil (tung oil) and its substitute, (dehydrated castor oil,) have largely replaced linseed oil in modern oil varnishes.

Varnishes usually contain 40 to 60% film-forming solids. Interior types are low in drying oil and usually contain low-odor solvents.

Varnish vehicles are used in making high grade enamels, and most interior paints use some variation of varnish as the vehicle.

The definitive elements of enamel paints are a varnish-type vehicle, low P.V.C., and high gloss. The range of P.V.C. for enamels is usually 18 to 35%. The percentage of F.F.S. is somewhat lower than in other paints, and the pigment is usually ground considerably finer than in other paints. Since the P.V.C. is low, higher hiding-strength pigments are required. Pigments are usually of the non-chalking types.

The definition above is also rather primordial because so-called painter's enamels may be simply paints having high gloss but slightly higher P.V.C.'s. Also, since many paints now use resins and bodied oils in combination with unbodied oil, the majority of paint vehicles are, at least in part, varnish-type vehicles.

Floor enamels usually use as much pigment, as reinforcement against abrasion, as possible and still preserve a high gloss.

Paints as Protection Against Corrosion

Paints are really about the most durable of all commonly used engineering materials; concrete, steel, wood, etc., are all attacked more readily by the "elements" of nature. Paints, then, provide a rather miraculous protective shield against the ravaging elements. It has been emphasized earlier that iron will not rust in dry air and that moisture is therefore an agent of corrosive destruction. A paint film may therefore

prevent rusting by simply providing a moisture-proof envelope, capsule, or barrier around the article. Yet, if this envelope becomes punctured, moisture may gain easy access, be captured, or even held in reserviors within the envelope.

Paint films, too, are eventually eroded or corroded away, but fortunately this is usually a slow, gentle, attrition of the surface and is often called chalking. Self-cleaning paints naturally have higher chalking rates than paints such as machinery enamels, bridge paints, or automobile finishes which are usually of the slow-or non-chalking variety.

Unless surfaces are especially prepared by grinding, polishing, or other smoothing operations, they are usually rough and mountainous in relation to the thickness of paint films. These mountains protrude into the paint films and are the points first exposed by normal chalking or abrasions. Whereas the average thickness of films might be six or eight mils, the thicknesses over these mountains may be only 2 or 3 mils. Thin films are more permeable to moisture, deteriorate more rapidly, and, are in effect, weak spots in the barrier. Rust forming under a thin or punctured paint film has a volume two to eight times greater than the parent iron. This action results in the formation of rust blisters which further aggravate the corrosion process. Surface roughness is therefore an obvious detriment to the durability of paints. Moreover, the excellent durability of automobile finishes has, at times, been credited to careful smoothing of the metal surfaces.

The envelope concept would imply that the paints do not necessarily form adherent films. Such might actually be the case if, for instance,

the surface were oily or not properly prepared at the time of painting. However, it is essential that paints be strongly adherent and that the adhesive bond to such that, should a lesion or puncture develop in the film, there would be no invasion of moisture under the paint at the intervening boundary or exposed interface. It follows, therefore, that paints should intimately wet the surfaces to which they are applied. Much of the long-standing merits of linseed oil as a primer vehicle is credited to the fact that it effectively wets iron or steel surfaces despite minor rust or scale. Purified linseed oils therefore are used extensively, even in oil-alkyd primer vehicles, to enhance wetting.

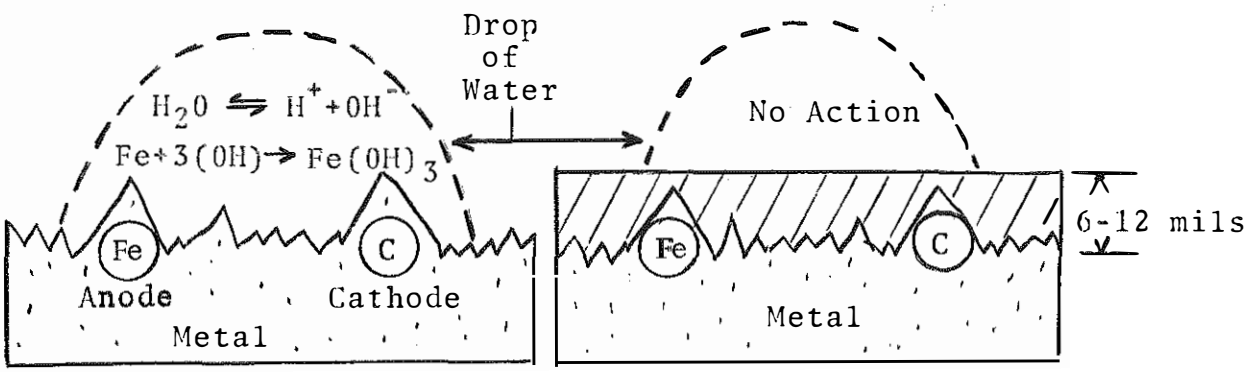
The importance of adhesion may be further emphasized by directing attention to the performance in recent years of finishes on home appliances and automobiles. Formerly, if these finishes became scratched, rust often spread rather rapidly; whereas, with phosphate treatment of the metal or "Bonderizing," the encroachment of rust under the paint film has been considerably retarded.

Coupled with the impermeability of paint binders to moisture, the chemical reactivity of the pigment with the binder and metal is of great importance. For instance, pigments which are highly soluble in water would not be satisfactory at all. Certain pigments, however, such as red lead, lead chromate, zinc chromate, blue lead, zinc dust, and strontium chromate are known to act as rust-inhibitors. They are sometimes credited with an ability to preserve a certain amount of alkalinity and to react with organic acids within or present as oxidation products of the binder and to produce

insoluble soaps which then tend to enhance adhesion and to prevent the paint films from becoming too brittle. Those who have had the misfortune to have painted new, untreated, galvanized guttering and downspouts or untreated aluminum with ordinary house paints may fully appreciate the folly of it all. Zinc soaps are, of course, obvious detriments to the adhesion of paint films. The most successful pretreatments of zinc and aluminum, as assurance against such loss of adhesion, usually involves de-greasing or de-oiling, etching, and phosphating or chromatizing of the surfaces. Failures due to loss of adhesion on metals are usually explainable on the basis of soluble pigments or the soaps formed therefrom. It is for this reason too that zinc oxide is not used in under coats for painting new wood, but is used extensively in finish coats.

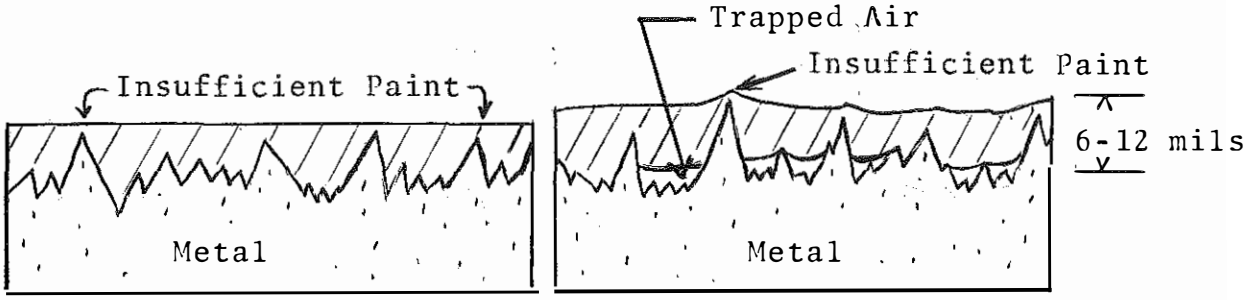
There are, of course, several mechanisms attendant to corrosion. For instance, it is thought that soluble pigments at or near the interface may induce electro-endosmosis, that graphite carbon or other undissolved materials in the metal surface may create galvanic cells, and that localized moisture and oxygen may create concentration cells. All are destructive, but all may be minimized by the proper design of paints and their proper application. On metals, the minimum safe thickness of good paint is about 6 mils. Assuming that 10 mils are applied and assuming that the normal chalking rate is about .3 mils per year, then it might be expected that 13 years of service could be obtained before repainting would be needed.

Some of the features thus described herein are illustrated by schematic drawings.



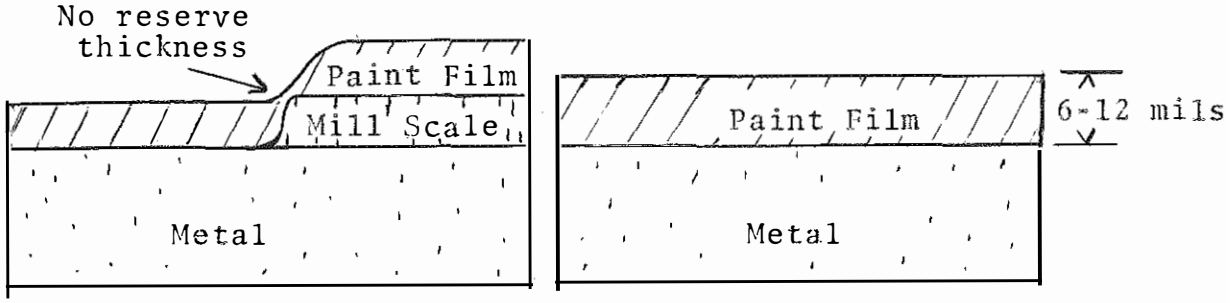
Chemical Mechanism of Rusting Unprotected Metal

Protected Metal



Excellent Wetting but Rough Surface

Poor Wetting Rough Surface



Uneven Thickness due to Mill Scale

Smooth Surface Uniform Thickness of Paint